
Time-Dependent Density Functional Theory as a Foundation for a Firmer Understanding of Sum-Over-States Density Functional Perturbation Theory: “Loc.3” Approximation

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ABSTRACT: Sum-over-states density functional perturbation theory (SOS-DFPT) (Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J Am Chem Soc* 1994, 116, 5898) has been successful as a method for calculating nuclear magnetic resonance (NMR) chemical shifts. The key to this success is the introduction of an ad hoc correction to the excitation energies represented by simple orbital energy differences in uncoupled density functional theory. It has been suggested (Jamorski, C.; Casida, M. E.; Salahub, D. R. *J Chem Phys* 1996, 104, 5134) that the good performance of this methodology could be partly explained by the resemblance of the corrected excitation energy to the orbital energy difference given by time-dependent density functional theory (TDDFT). In fact, according to exact (wave function) time-dependent perturbation theory, both magnetic and electric perturbations may be described using essentially the *same* simple SOS expression. However in adiabatic TDDFT, with no explicit relativistic or current density functional dependence, the functional is approximate and so the magnetic and electric SOS expressions are different. Because

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TDDFT (neglecting relativistic and current density functional dependence) is formally exact for electric perturbations but not magnetic perturbations and because the two SOS expressions should have the same form, we propose that *the SOS expression for electric perturbations should also be used for magnetic perturbations*. We then go on to realize our theory by deriving a “Loc.3” approximation that is explicitly designed by applying the electric field SOS expression to magnetic fields within the two-level model and Tamm–Dancoff approximation. Test results for 13 small organic and inorganic molecules show that the Loc.3 approximation performs at least as well as the “Loc.1” and “Loc.2” approximations of SOS-DFPT. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 91: 67–83, 2003

Key words: sum-over-states density functional perturbation theory; NMR chemical shifts; time-dependent DFT; magnetic perturbations

1. Introduction

The general importance of nuclear magnetic resonance (NMR) for the study of large molecules has continued to fuel the search for new ways to calculate NMR shielding constants [1–8]. The challenge here is to find a computational method that is simultaneously rigorous, computationally efficient, and reliable in comparison with experiment. Sum-over-states density functional perturbation theory (SOS-DFPT), as implemented in DEMON-NMR by Malkin and coworkers [9], offers one efficient alternative to expensive *ab initio* methods such as second-order Møller–Plesset perturbation theory (MP2) and coupled-cluster (CC) methods. However, the reliability of SOS-DFPT depends, in part, on the introduction of an ad hoc correction to the uncorrected excitation energy initially calculated as a simple orbital energy difference (“uncoupled theory”). Following the original article [9], this excitation energy correction is termed either “Loc.1” or “Loc.2,” depending upon the particular choice of correction. Despite the ad hoc nature of this correction, it has been difficult to design a more rigorous approach that performs as well as SOS-DFPT within the context of density functional theory (DFT) (see, e.g., [10].) In this article, we suggest why the SOS-DFPT performs as well as it does by showing how a similar theory can be derived within the rigorous framework of time-dependent DFT (TDDFT) without the use of either relativity or current density functional. In so doing, we elaborate on a previous observation [11] that the singlet–singlet excitation energy in a two-state model calculated with TDDFT offers support for the approximations to the excitation energy made in SOS-DFPT.

Neither relativistic DFT nor current DFT (CDFT) are used in the present work. Instead, we rely on the fact that electric and magnetic perturbations can be treated in principle in an exact theory by using formally identical SOS expressions. However, in the absence of relativistic DFT or CDFT, approximate exchange correlation functionals lead to different TDDFT expressions for electric and magnetic perturbations. We show how this dilemma can be circumvented by using the Tamm–Dancoff approximation (TDA) and how this can subsequently be used to derive rigorous SOS-DFPT expressions that agree as well with high-quality *ab initio* calculations as does the previous ad hoc theory, consistent with the previous good results for dynamic polarizabilities and excitation energies obtained from TDDFT. This provides us with a comprehensive formulation of SOS-DFPT and TDDFT in which the electric and magnetic fields are placed on the same footing.

This article is organized as follows. SOS-DFPT is derived from TDDFT in Section 2. This leads to the “Loc.3” correction. Computational details will be given in Section 3. In Section 4, we present evidence that the Loc.3 approximation does indeed perform as well as the Loc.1 and Loc.2 approximations (and better than the uncoupled approximation.) Section 5 provides a concluding discussion.

2. Theoretical Background

The DFT of NMR chemical shifts is usually explained in terms of the exact sum-over-states (SOS) expansion describing the initial linear response of a molecule to a perturbation. We will review this briefly and then show why we think that there is some degree of liberty in how SOS theory is used in DFT.

2.1. SOS EXPRESSIONS

The clearest derivation of the SOS expression in linear response theory comes from time-dependent perturbation theory (see, e.g., Ref. [12]). It can be shown (Appendix A) that for a molecule initially in its ground stationary state Ψ_0 the linear response of the property described by a one-electron operator, \hat{a} , to a time-dependent perturbation, $\hat{b} \cos \omega t$, has the form

$$\delta\langle\hat{a}\rangle(t) = \delta\langle\hat{a}\rangle_1(\omega)\sin \omega t + \delta\langle\hat{a}\rangle_2(\omega)\cos \omega t. \quad (2.1)$$

Here, the coefficients $\delta\langle\hat{a}\rangle_1(\omega)$ and $\delta\langle\hat{a}\rangle_2(\omega)$ are given by the SOS formulae

$$\delta\langle\hat{a}\rangle_1(\omega) = \sum_{I \neq 0} \frac{2\omega_I \text{Im}\langle\Psi_0|\hat{a}|\Psi_I\rangle\langle\Psi_I|\hat{b}|\Psi_0\rangle}{\omega_I^2 - \omega^2} \quad (2.2)$$

and

$$\delta\langle\hat{a}\rangle_2(\omega) = \sum_{I \neq 0} \frac{2\omega_I \text{Re}\langle\Psi_0|\hat{a}|\Psi_I\rangle\langle\Psi_I|\hat{b}|\Psi_0\rangle}{\omega^2 - \omega_I^2}. \quad (2.3)$$

Here, $\hbar\omega_I = E_I - E_0$ (and $\hbar = 1$) and E_I and Ψ_I refer, respectively, to excited-state energies and wave functions. In most cases of interest, the product $\hat{a}\hat{b}$ is real and only $\delta\langle\hat{a}\rangle_2(\omega)$ is of interest. Moreover, $\delta\langle\hat{a}\rangle_1(\omega)$ vanishes in the static limit. In what follows, we will be concerned exclusively with $a(\omega) = \delta\langle\hat{a}\rangle_2(\omega)$. The static limit of $a(\omega)$ is explicitly

$$a = -2 \sum_{I \neq 0} \frac{\text{Re}\langle\Psi_0|\hat{a}|\Psi_I\rangle\langle\Psi_I|\hat{b}|\Psi_0\rangle}{\omega_I}. \quad (2.4)$$

Concrete examples of SOS expressions include the dynamic polarizability, describing the linear response of the dipole moment to an applied dipole electric field,

$$\alpha_{x,z}(\omega) = \sum_{I \neq 0} \frac{2\omega_I \langle\Psi_0|\hat{x}|\Psi_I\rangle\langle\Psi_I|\hat{z}|\Psi_0\rangle}{\omega_I^2 - \omega^2}, \quad (2.5)$$

and the paramagnetic component of the NMR chemical shift tensor,

$$\sigma_{x,z}^p(N) = -2 \sum_{I \neq 0} \frac{\text{Re}\langle\Psi_0|\hat{h}_x^{\text{pso}}(N)|\Psi_I\rangle\langle\Psi_I|\hat{h}_z^{\text{orb}}|\Psi_0\rangle}{\omega_I}, \quad (2.6)$$

where $\hat{h}_z^{\text{orb}} = \hat{l}_z$ is the z -component of the angular momentum operator and $\hat{h}_x^{\text{pso}}(N) = (1/c^2)\hat{l}_x^N r_N^{-3}$ is the paramagnetic spin-orbital operator for nucleus N . Here, r_N is the distance of the electron from nucleus N and \hat{l} is the angular momentum operator. For simplicity of notation, we have only written the (x, z) components but the other components are strictly analogous. The complete expression for the chemical shift tensor is

$$\sigma_{x,z}(N) = \sigma_{x,z}^d(N) + \sigma_{x,z}^p(N), \quad (2.7)$$

where the diamagnetic component is given by

$$\sigma_{x,z}^d(N) = -\langle\Psi_0|xz_A r_A^{-3}|\Psi_0\rangle, \quad (2.8)$$

with an additional contribution of $\langle\Psi_0|\vec{r} \cdot \vec{r}_A r_A^{-3}|\Psi_0\rangle$ for the diagonal elements of the diamagnetic component.

2.2. TDDFT RESPONSE THEORY

The SOS expressions given in Section 2.1 assume that the exact energies and wave functions of the unperturbed system are known. These expressions cannot be used directly in quantum chemical applications of DFT for two reasons: First, DFT is normally formulated without any explicit reference to the exact wave function; second, any wave function that does appear in quantum chemical applications of DFT is necessarily approximate in so far as it is expressed in a finite basis set. Nevertheless, SOS expressions analogous to the exact expressions of Section 2.1 can be derived from TDDFT for quantum chemical applications.

In TDDFT, the linear response of the Kohn-Sham density matrix, $\delta\vec{P}$, to an applied time-dependent perturbation, $\delta\vec{v}_{\text{appl}}$, is given by the equation [12]

$$\left\{ \omega \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} - \begin{bmatrix} A & B \\ B & A \end{bmatrix} \right\} \begin{pmatrix} \delta\vec{P}(\omega) \\ \delta\vec{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} \delta\vec{v}_{\text{appl}}(\omega) \\ \delta\vec{v}_{\text{appl}}^*(\omega) \end{pmatrix}, \quad (2.9)$$

where

$$A_{ia\sigma, jb\tau} = \delta_{i,j} \delta_{a,b} \delta_{\sigma,\tau} (\epsilon_{a\sigma} - \epsilon_{i\tau}) + K_{ia\sigma, jb\tau} \quad (2.10)$$

and

$$B_{ia\sigma, jb\tau} = K_{ia\sigma, bj\tau}. \quad (2.11)$$

Here, $\epsilon_{a\sigma}$ and $\epsilon_{b\tau}$ are Kohn–Sham orbital energies and $K_{ia\sigma,jb\tau} = \delta v_{ia\sigma}^{\text{SCF}} / \delta P_{jb\tau}$ is the coupling matrix describing the linear response of the self-consistent field (SCF) to a change in the Kohn–Sham density matrix. In the case of the dynamic polarizability, the perturbation is real and a little linear algebra (Appendix B) then leads to

$$\alpha_{x,z}(\omega) = 2\tilde{x}^\dagger(\mathbf{A} - \mathbf{B})^{1/2} \times [(\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2} - \omega^2\mathbf{1}]^{-1} \times (\mathbf{A} - \mathbf{B})^{1/2}\tilde{z}. \quad (2.12)$$

In the case of the paramagnetic contribution to the NMR chemical shift tensor, the perturbation is purely imaginary and we are dealing with $Im\delta\tilde{P}(\omega)$ and $Im\delta\tilde{v}_{\text{appl}}(\omega)$. After some linear algebra (Appendix B), it can be shown that

$$\sigma_{x,z}^p(\omega; N) = -2[(\tilde{h}^{\text{ps0}})_x(N)]^\dagger(\mathbf{A} + \mathbf{B})^{1/2} \times [(\mathbf{A} + \mathbf{B})^{1/2}(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})^{1/2} - \omega^2\mathbf{1}]^{-1} \times (\mathbf{A} + \mathbf{B})^{1/2}\tilde{h}_z^{\text{orb}}. \quad (2.13)$$

According to the exact SOS equations of Section 2.1, the dynamic polarizability and paramagnetic part of the NMR chemical shift both have poles at the excitation energies of the system. From Eq. (II.12) this is when

$$(\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2}\tilde{F}_1 = \omega^2\tilde{F}_1. \quad (2.14)$$

This is the equation normally solved in quantum chemical implementations of TDDFT because the matrix $\mathbf{A} - \mathbf{B}$ is diagonal for generalized gradient approximations [12]. The corresponding excitation energy equation deduced from Eq. (2.13) is

$$(\mathbf{A} + \mathbf{B})^{1/2}(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})^{1/2}\tilde{F}_2 = \omega^2\tilde{F}_2. \quad (2.15)$$

Equations (2.14) and (2.15) are easily seen to be equivalent by setting $\tilde{F}_2 = [(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})]^{-1/2}\tilde{F}_1$. Naïvely it might seem as though we could just replace \tilde{x} and \tilde{z} in the dynamic polarizability expression [Eq. (2.12)] with $(\tilde{h}^{\text{ps0}})_x(N)$ and \tilde{h}_z^{orb} to obtain the expression for the paramagnetic part of the chemical shift [Eq. (2.13)], but this is not the case because the real and imaginary parts of the transition density matrices figuring in the SOS expressions are different. A priori only the electric form is correct because TDDFT at this level is only formally justified for electric perturbations.

Nevertheless, it is interesting to remark that both the magnetic and electric forms become once again equivalent within the TDA, which consists of setting $\mathbf{B} = \mathbf{0}$. Then, the excitation energies are given by

$$\mathbf{A}\tilde{F}_1 = \omega\tilde{F}_1, \quad (2.16)$$

and

$$\alpha_{x,z}(\omega) = 2\tilde{x}^\dagger\mathbf{A}^{1/2}(\mathbf{A}^2 - \omega^2\mathbf{1})^{-1}\mathbf{A}^{1/2}\tilde{z} \quad (2.17)$$

$$\sigma_{x,z}^p(\omega; N) = -2[(\tilde{h}^{\text{ps0}})_x(N)]^\dagger\mathbf{A}^{1/2} \times [\mathbf{A}^2 - \omega^2\mathbf{1}]^{-1}\mathbf{A}^{1/2}\tilde{h}_z^{\text{orb}}, \quad (2.18)$$

which reduce to

$$\alpha_{x,z} = 2\tilde{x}^\dagger\mathbf{A}^{-1}\tilde{z} \quad (2.19)$$

$$\sigma_{x,z}^p(N) = -2[(\tilde{h}^{\text{ps0}})_x(N)]^\dagger\mathbf{A}^{-1}\tilde{h}_z^{\text{orb}} \quad (2.20)$$

in the static limit. The TDA is well established in Hartree–Fock-based theory and there is now considerable evidence that the TDA normally has only a minor effect on excitation spectra of molecules near their equilibrium geometries and can actually improve the description of excitation energies at deformed geometries, near points of instability of the ground-state wave function [13, 14]. We will use this result in Section 2.3 to develop the Loc.3 approximation.

2.3. SOS DENSITY-FUNCTIONAL-PERTURBATION THEORY

We are now in an excellent position to understand SOS-DFPT. Traditional Hohenberg–Kohn–Sham DFT applies only to external potentials that are simple coordinate-dependent multiplicative functions. This applies to the electric field case but not to the general magnetic field case. Treatment of this latter case would seem to require either a relativistic reformulation of DFT or the use of functionals that depend upon the current density as well as the charge density. Neither was done in SOS-DFPT. Instead, an approximation was sought using traditional density functionals that contain no current density dependence.

Direct application of Eq. (2.13) leads to

TABLE I
Comparison of excitation energy corrections to simple orbital energy differences obtained from various theories within the two-level model.

Ansatz	$\Delta E_{i \rightarrow a}^{xc}$
UKS ^a	No correction
Ab initio	
CIS ^b	$2K_{ia} - J_{ia}$
IVO ^c	$2K_{ia}$
DFT	
Loc. 1	$-\int \rho_i(\mathbf{r}) \frac{\delta \epsilon_{xc}^{\text{LDA}}(\mathbf{r})}{\delta \rho_{\uparrow}(\mathbf{r})} \rho_a(\mathbf{r}) d\mathbf{r}$
Loc. 2	$-\int \rho_i(\mathbf{r}) \frac{\delta v_{xc}^{\uparrow, \text{LDA}}(\mathbf{r})}{\delta \rho_{\uparrow}(\mathbf{r})} \rho_a(\mathbf{r}) d\mathbf{r}$
Loc. 3	$2K_{ia} + \int \rho_i(\mathbf{r}) \left(\frac{\delta v_{xc}^{\uparrow, \text{LDA}}(\mathbf{r})}{\delta \rho_{\uparrow}(\mathbf{r})} + \frac{\delta v_{xc}^{\downarrow, \text{LDA}}(\mathbf{r})}{\delta \rho_{\downarrow}(\mathbf{r})} \right) \rho_a(\mathbf{r}) d\mathbf{r}$

^a Uncoupled Kohn–Sham.

^b Singles configuration interaction. Equivalently the TDA applied to time-dependent Hartree–Fock.

^c Improved virtual orbital [15, 16], basically the same as the static exchange approximation (reviewed in Ref. [17]). Note how the use of relaxed Hartree–Fock orbitals leads to the elimination of the Coulomb integral J_{ia} .

$$\sigma_{x,z}^p(N) = -2 \sum_{i \in \text{occ}, a \in \text{virt}} \frac{\text{Re} \langle \psi_i | \hat{h}_x^{\text{psO}}(N) | \psi_a \rangle \langle \psi_a | \hat{h}_z^{\text{orb}} | \psi_i \rangle}{\omega_{i \rightarrow a}}, \quad (2.21)$$

where the excitation energy

$$\omega_{i \rightarrow a} = \epsilon_a - \epsilon_i + \Delta E_{i \rightarrow a}^{xc} \quad (2.22)$$

corresponds to the uncoupled approximation ($\Delta E_{i \rightarrow a}^{xc} = 0$ in Table I). This already turns out to work fairly well in approximating chemical shifts [18]. However, two nonzero ad hoc corrections to $\omega_{i \rightarrow a}$, called “Local 1” (Loc.1) and “Local 2” (Loc.2) in Ref. [18], have been shown to provide significant reductions in the errors of computed chemical shifts compared to experiment. In fact, Wilson et al. [10] recently confirmed that excitation corrections as little as 0.4 eV can have a large influence on predicted magnetic properties.

To understand why such corrections are so important for quantitative prediction of NMR shielding tensors, let us consider a peculiar “magnetic spectrum,” namely, that obtained by plotting the

individual terms in the SOS expression for the paramagnetic contribution to the shielding tensor [Eq. (2.6)] (i.e., the product of the expectation values of \hat{h}^{psO} and \hat{h}^{orb}) against the corresponding excitation energy in the denominator. The result is shown in Figure 1 for CH₂O. It is evident that the individual contributions from different excitation energies to the σ^p term are distributed in an almost symmetrical fashion around the zero line. This means that a great deal of cancellation occurs in calculating σ^p and hence that there is a delicate balance between positive and negative terms, which together must somehow sum up to obtain a reasonable value. This strongly suggests that part of “getting the right answer for the right reason” is getting good singlet excitation energies, $\omega_{i \rightarrow a}$, in the denominator in Eq. (2.6), something that has already been demonstrated to be possible through TDDFT.

In this article, we suggest that one rigorous way to improve upon DFT methodology for calculating NMR chemical shifts without recourse to either relativistic DFT or current DFT can be based upon the fact that traditional Hohenberg–Kohn–Sham DFT is formally exact in the electric field case and that in practice good results for dynamic polarizabilities and excitation energies are being obtained from TDDFT in the electric field case. Hence, we

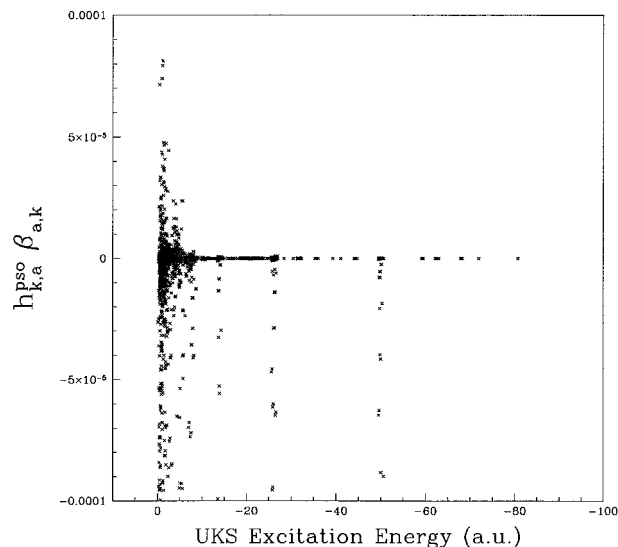


FIGURE 1. On the y-axis is plotted half the value of the $l = (k,a)$ term of the summation in Eq. (2.6); in the x-axis are reported the relative excitation energies (a.u.). The data correspond to a ¹³C chemical shift calculation on CH₂O performed with LDA exchange correlation potential within the uncoupled Kohn–Sham approximation; the basis set used is III-IGLO.

seek a formulation of TDDFT in which the electric and magnetic fields are placed on the same footing. One way to do this is to simply use the electric field form of TDDFT response theory for magnetic perturbations. In practice, we actually use the fact that, as shown in Section 2.2, the TDA [Eqs. (2.17) and (2.18)] provides equivalent formulae for magnetic and electronic perturbations.

To facilitate comparison with the SOS-DFPT expression [Eq. (2.21)], we will also assume that the two-level model (2LM) applies, so that each transition may be approximated by promotions from an occupied orbital ψ_i to an unoccupied orbital ψ_a to form the singlet state $\Psi_{i \rightarrow a} = (1/\sqrt{2})(\hat{a}_a^\dagger \hat{a}_i \uparrow + \hat{a}_a^\dagger \hat{a}_i \downarrow)\Psi_0$. Once this is done, we obtain the (new) Loc.3 approximation given in Table I. Note that (contrary to what is stated in Ref. [18]) the fact that we treat Ψ_0 as the monodeterminantal Kohn–Sham wave function is *not* an approximation but follows directly from TDDFT.

Comparison of the Loc.1, Loc.2, and Loc.3 formulae shows that they are all different types of exchange or exchange correlation integrals. As such, they might be expected to give similar results (and they do!); however, Loc.3 is firmly grounded in TDDFT and gives us hope that any improvements in our understanding of how to calculate excitation energies from TDDFT will be reflected in subsequent improvements of NMR chemical shifts.

3. Computational Details

All calculations have been performed within the DEMON suite of programs. In particular, the self-consistent solution of the Kohn–Sham equations was performed with Version 3.5 of DEMON-KS [19]; TDDFT calculations were performed with a modified version (3.1) of DEMON-DYNARHO; and NMR shielding tensor calculations were performed with a slightly modified version (1.2) of DEMON-NMR [9, 18].

In DEMON-NMR the gauge origin problem is solved by using the individual gauge for localized orbitals (IGLO) method developed by Kützelnigg et al. [1]. We follow the recommendations of Malkin and coworkers [9, 18] and use the III-IGLO orbital basis set for all atoms.

DEMON-KS and DEMON-DYNARHO make use of numerical grids and sets of auxiliary basis functions to evaluate exchange correlation integrals and eliminate four center integrals. The same grids and auxiliary basis functions were used in running the two

programs. For the grid, we used the EXTRAFINE option (194 points per radial shell) in combination with a 64-point radial grid. The auxiliary basis functions used were taken from the DEMON basis set library. Specifically, they are the (5, 2; 5, 2) set for carbon, nitrogen, oxygen, and fluorine and (5, 1; 5, 1) for hydrogen.

Several exchange correlation functionals have been used to establish their effect on calculated NMR shielding tensors. For the local density approximation (LDA), we use the Vosko, Wilk, and Nusair (VWN) parameterization of the exchange correlation functional [20]. Generalized gradient approximations used were the 1986 exchange-only functional of Perdew and Wang [21] combined with the 1986 correlation functional of Perdew [22] (together these two functionals will be referred to as PD86) and the 1991 functional of Perdew and Wang (PD91) [23]. We also used the asymptotically corrected LDA (AC-LDA), which is obtained from the LDA by introducing a constant shift to incorporate the effect of derivative discontinuity and a spliced asymptotic correction in the large r region [24, 25]. The constant shift required to bring the LDA functional inline with the exact potential is given by the difference between the energy of the highest occupied molecular orbital (HOMO) calculated with the LDA functional and the exact HOMO energy, ω_H , which in practice is approximated as minus the ionization potential calculated as the difference of total energies obtained from two self-consistent LDA calculations, one on the N electron system and the other on the $N - 1$ electron system (Δ SCF method),

$$\Delta = \epsilon_H^{\text{LDA}} - \omega_H. \quad (3.1)$$

For the asymptotic region the correct behavior is obtained combining the shifted LDA exchange correlation potential in the bulk region with the van Leeuwen Baerends potential (LB94) [26] in the large r region, taking the switchover point between the two potentials to be where they cross,

$$v_{xc}^{\text{AC-LDA}}(r) = \text{Max}[v_{xc}^{\text{LDA}}(r) - \Delta, v_{xc}^{\text{LB94}}(r)] \quad (3.2)$$

4. Results

In this section, we compare the behavior of the more rigorous Loc.3 correction with that of the previous ad hoc Loc.1 and Loc.2 corrections for use

TABLE II
Mean absolute error ($\bar{\delta}$) calculated for the different exchange correlation functionals.

	Mean absolute error, $\bar{\delta}$ (ppm)			
	UKS	Loc.1	Loc.2	Loc.3
LDA				
C, N, O, F	29.6	15.0	11.0	12.7
H	0.9	0.9	1.2	0.8
AC-LDA				
C, N, O, F	30.4	23.9	22.4	20.4
H	0.6	0.5	0.5	0.4
PD86				
C, N, O, F	23.7	11.0	10.3	9.2
H	0.5	0.4	0.4	0.4
PD91				
C, N, O, F	18.2	7.4	8.0	10.0
H	0.5	0.5	0.4	0.4

in the SOS-DFPT calculation of NMR chemical shifts. To do this, we have chosen the linearized coupled cluster doubles (L-CCD) values of Cybulski and Bishop [27] as reference values. The geometries used in our calculations are the same as those reported by Cybulski and Bishop. The NMR chemical shifts are for the nuclei ^1H , ^{13}C , ^{17}O , ^{15}N , and ^{17}F .

Mean absolute errors ($\bar{\delta}$) calculated by the equation

$$\bar{\delta} = \frac{1}{N} \left(\sum_i^N |\sigma_i^{\text{Calc.}} - \sigma_i^{\text{L-CCD}}| \right), \quad (4.1)$$

are given in Table II. Here, N is the total number of the test molecules, $\sigma_i^{\text{Calc.}}$ is the value of the isotropic shielding calculated for the i th test molecule, and $\sigma_i^{\text{L-CCD}}$ is the value of the isotropic shielding for the i th molecule calculated with the L-CCD methodology [27]. Table II confirms that the rigorous Loc.3 correction performs, on average, as well as the ad hoc Loc.1 and Loc.2 corrections, all of which perform better than the UKS theory. Different values are also given in Table II for different choices of functionals for the exchange correlation potential, v_{xc} . Because the Loc.1, Loc.2, and Loc.3 corrections are always calculated using the LDA, the most consistent choice is undoubtedly to use the LDA v_{xc} . In this particular case, the Loc.3 correction appears to be the best compromise for NMR chemical shifts for both heavy atoms (C, N, O, F) and hydrogen. As pointed out in the original SOS-DFPT article [9],

improved results can be obtained by using a v_{xc} obtained via a generalized gradient approximation (GGA). Table II confirms this in the case of the PD86 and PD91 functionals. For the PD86 functional, the Loc.3 correction appears to slightly outperform the Loc.1 and Loc.2 corrections. For the PD91 functional, the ad hoc Loc.1 functional seems to be the best compromise for NMR chemical shifts for both heavy atoms (C, N, O, F) and hydrogen.

Surprisingly, the AC-LDA gives inferior results compared with those of the simple LDA, regardless of the choice of excitation energy correction, despite the fact that the AC-LDA gives a better excitation spectrum [14]. A similar result was found by Wilson et al. [10]. As pointed out earlier (Fig. 1), the relation between excitation energies and the paramagnetic component of the isotropic chemical shift is not simple. However, it is known that the asymptotic correction leads to a better spacing of the excitation energies by avoiding a variational collapse due to an artificially low ionization threshold [14]. Naïvely this would be expected to increase the average denominators in the SOS expression Eq. (2.21), hence producing the observed decrease in the magnitude of the paramagnetic component. This may also simply be an indication of the importance of using a consistent functional for both v_{xc} and the Loc. corrections.

Figure 2 provides a graphical overview of errors in the different approximations for chemical shifts. Not a repetition of Table II, Figure 2 shows that there are at least four points above about 200 ppm that are well approximated regardless of what excitation energy correction is used. These are the heavy atom shifts for CH_4 , NH_3 , H_2O , and HF , and a similar statement can be made about their hydrogen shifts and for H_2 . The real differences occur for the unsaturated molecules C_2H_2 , CH_2O , HNC , HCN , CO , F_2 , and N_2 , although important differences between different excitation energy approximations are also seen for H_2O_2 . Unsaturated molecules have lower-lying valence-type excitations, absent in the simple saturated molecules, which are dominated by Rydberg-type excitations. Thus, it is not entirely surprising from an SOS point of view that the unsaturated molecules are the most sensitive to corrections to the excitation energies.

Tables III–VI provide a detailed quantitative comparison between the effect of different excitation energy corrections and different functionals for v_{xc} for isotropic shielding constants. For the LDA, the Loc.3 approximation performs on average as

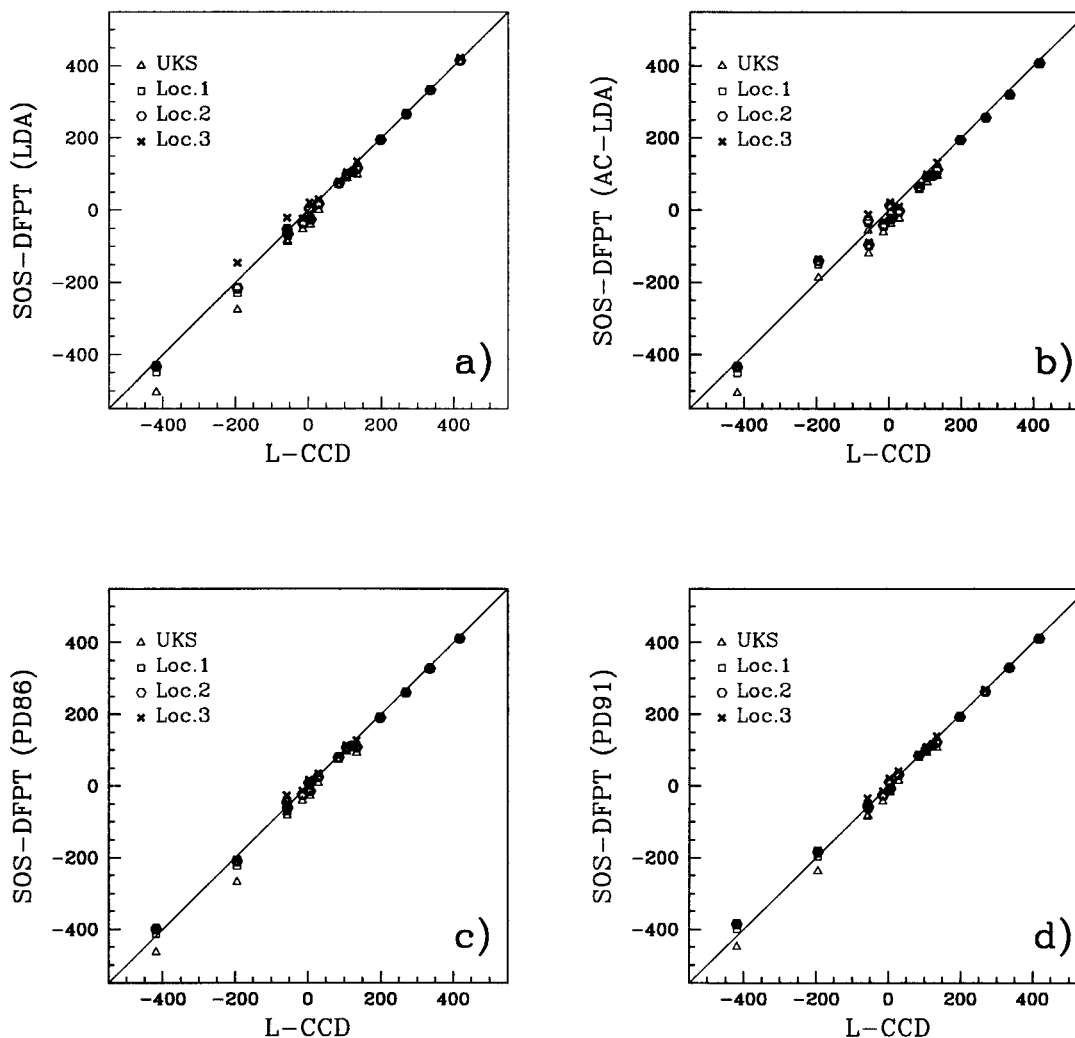


FIGURE 2. Absolute isotropic shielding data for ^{13}C , ^{15}N , ^{17}O , and ^{19}F calculated with different exchange correlation potentials and LDA v_{xc} plotted against the corresponding L-CCD reference values: (a), LDA; (b), AC-LDA; (c), PD86; (d), PD91. (Summary of detailed information is given in Tables III–VI.)

well as the Loc.1 and Loc.2 approximations. However, improved results are obtained from the Loc.3 approximation for H_2O_2 and HNC . The Loc.3 approximation has the same difficulty as the Loc.1 and Loc.2 approximations in reproducing the reference numbers for H_2CO and C_2H_2 . CO and F_2 are two examples where the Loc.3 performs worse than the Loc.1 and Loc.2 approximations when it comes to reproducing the L-CCD reference numbers. Similar trends are also observed for the two GGAs (PD86 and PD91), although for HNC the Loc.3 approximation is actually further from the L-CCD results than are the Loc.1 and Loc.2 approximations, which are already good. The AC-LDA isotropic chemical shift tensor is sometimes larger in

magnitude than the corresponding L-CCD value and sometimes smaller, but on average (as already mentioned) use of the AC-LDA v_{xc} leads to inferior isotropic chemical shifts.

5. Conclusion

The main objective of this article has been to show how the ad hoc Loc.1 and Loc.2 approximations of SOS-DFPT can be replaced by a more rigorous Loc.3 approximation derived via TDDFT. In particular, after having noted that the formal similarity of the electric and magnetic response theory expressions expected in an exact theory are *not*

TABLE III
Isotropic shielding σ calculated with the LDA exchange correlation potential within the IGLO approximation [1].

	Isotropic shielding, σ (ppm)						Ref. value ^b
	LDA				L-CCD ^a		
	UKS	Loc.1	Loc.2	Loc.3			
HCCH							
C	102.4	104.9	105.7	105.2	122.6	121.8	
H	29.7	29.6	29.6	29.6	30.6	—	
H ₂ CO							
C	-39.7	-29.0	-25.7	-24.8	6.1	8.2	
O	-504.9	-449.4	-432.5	-430.3	-418.0	-379.1	
H	20.3	20.7	20.8	20.8	22.6	22.4	
CH ₄							
C	193.3	194.4	194.8	194.3	198.6	198.9	
H	31.1	31.1	31.1	31.1	31.5	31.6	
H ₂ O ₂							
O	99.0	112.1	116.2	135.6	133.9	—	
H	23.7	24.0	24.1	24.5	25.3	—	
NH ₃							
N	263.9	265.4	265.8	264.6	268.8	270.7	
H	31.1	31.1	31.1	31.0	31.7	31.6	
H ₂ O							
O	330.1	332.3	333.1	335.6	335.9	337.9	
H	30.6	30.6	30.6	30.5	31.2	30.9	
HNC							
C	-0.5	13.9	18.2	28.9	28.5	—	
N	87.1	96.0	98.7	105.2	105.5	—	
H	27.1	27.1	27.1	27.1	28.3	—	
HCN							
C	67.7	73.0	74.6	78.4	86.4	86.3	
N	-54.2	-39.7	-35.2	-23.8	-14.4	-13.6	
H	28.4	28.3	28.3	28.2	29.4	29.0	
CO							
C	-16.9	-0.8	3.9	21.1	3.9	5.6	
O	-83.9	-60.1	-53.0	-20.9	-57.4	-52.9	
HF							
F	412.7	415.1	415.9	422.8	417.6	418.6	
H	29.0	28.9	28.9	28.6	29.4	29.2	
F ₂							
F	-275.3	-229.7	-215.7	-146.0	-194.5	-186.5	
N ₂							
N	-88.3	-71.4	-66.2	-64.1	-55.7	-58.1	
H ₂							
H	26.4	26.4	26.4	26.4	26.7	26.7	

^a From Ref. [27].

^b Introduced in [27] as reference values.

present in TDDFT expressions, we point out that this is expected because nonrelativistic TDDFT without any current density dependence is formally exact only for electric perturbations. However, because it is exact for electric fields and there

is a formal similarity that should hold in a correct (relativistic or current density dependent) theory, we feel that it is justified to use the electric field linear response expression in TDDFT for magnetic perturbations.

TABLE IV
Isotropic shielding σ calculated with the AC-LDA [14, 24] within the IGLO approximation [1].

	Isotropic shielding, σ (ppm)					Ref. value ^b
	ACLDA				L-CCD ^a	
	UKS	Loc.1	Loc.2	Loc.3		
HCCH						
C	92.4	95.2	96.1	95.6	122.6	121.8
H	30.1	30.0	30.0	30.0	30.6	—
H ₂ CO						
C	-37.0	-27.0	-23.9	-23.0	6.1	8.2
O	-506.1	-451.4	-434.8	-432.4	-418.0	-379.1
H	20.4	20.8	21.0	20.1	22.6	22.4
CH ₄						
C	193.4	194.6	195.0	194.9	198.6	198.9
H	31.5	31.5	31.5	31.5	31.5	31.6
H ₂ O ₂						
O	95.6	108.6	112.7	132.8	133.9	—
H	24.3	24.6	24.7	25.1	25.2	—
NH ₃						
N	256.4	258.1	256.6	257.7	268.8	270.7
H	31.4	31.5	31.5	31.5	31.7	31.6
H ₂ O						
O	317.8	320.4	321.2	320.0	335.4	337.9
H	31.1	31.1	31.1	31.1	31.2	30.9
HNC						
C	-23.9	-7.3	-2.5	10.3	28.5	—
N	78.5	88.9	92.0	99.8	105.5	—
H	27.5	27.5	27.5	27.5	28.3	—
HCN						
C	55.9	61.5	63.3	67.5	84.4	86.3
N	-61.3	-46.1	-41.4	-29.3	-14.4	-13.6
H	28.8	28.8	28.8	28.7	29.4	29.0
CO						
C	-5.3	9.0	13.2	22.0	3.9	5.6
O	-56.3	-35.1	-28.7	-11.0	-57.4	-52.9
HF						
F	404.6	407.2	408.3	406.3	417.6	418.6
H	29.4	29.4	29.3	29.4	29.4	29.2
F ₂						
F	-186.2	-150.3	-139.2	-135.0	-194.5	-186.5
N ₂						
N	-120.2	-101.0	-95.1	-88.8	-55.7	-58.1
H ₂						
H	26.3	26.3	26.3	26.3	26.7	26.7

^a From Ref. [27].^b Introduced in [27] as reference values.

A few more steps were necessary to go from this realization to the Loc.3 approximation for SOS-DFPT. The first was to make the TDA. As in time-dependent Hartree-Fock theory, there is now considerable evidence that the TDA normally has only a minor effect on excitation spec-

tra of molecules near their equilibrium geometries and can actually improve the description of excitation energies at deformed geometries, near points of instability of the ground-state wave function [13, 14]. In this case, it also allows us to recover the formal similarity of the electric and

TABLE V
Isotropic shielding σ calculated with the PD86 exchange correlation potential within the IGLO approximation [1].

	Isotropic shielding, σ (ppm)					L-CCD ^a	Ref. value ^b
	PD86						
	UKS	Loc.1	Loc.2	Loc.3			
HCCH							
C	108.4	110.7	111.5	110.9	122.6	121.8	
H	30.1	30.0	30.0	30.0	30.6	—	
H ₂ CO							
C	-28.4	-18.8	-15.8	-15.1	6.1	8.2	
O	-463.7	-413.7	-398.4	-396.7	-418.0	-379.1	
H	21.0	21.4	21.5	21.5	22.6	22.4	
CH ₄							
C	188.6	189.8	190.1	189.8	198.6	198.9	
H	31.5	31.5	31.5	31.5	31.5	31.6	
H ₂ O ₂							
O	91.1	104.2	108.3	127.7	133.9	—	
H	24.3	24.7	24.8	25.2	25.2	—	
NH ₃							
N	258.6	260.2	260.7	259.5	268.8	270.7	
H	31.6	31.6	31.6	31.6	31.7	31.6	
H ₂ O							
O	324.4	326.8	327.5	326.1	335.4	337.9	
H	31.2	31.2	31.2	31.2	31.2	30.9	
HNC							
C	7.9	21.2	25.2	35.0	28.5	—	
N	96.2	104.6	107.1	113.1	105.5	—	
H	27.4	27.4	27.5	27.5	28.3	—	
HCN							
C	72.5	77.5	79.0	82.5	84.4	86.3	
N	-41.9	-28.2	-24.0	-13.4	-14.4	-13.6	
H	28.7	28.7	28.7	28.6	29.4	29.0	
CO							
C	-11.6	3.5	8.0	17.3	3.9	5.6	
O	-74.8	-51.9	-45.0	-26.1	-57.4	-52.9	
HF							
F	408.7	411.2	412.0	410.4	417.6	418.6	
H	29.8	29.7	29.6	29.7	29.4	29.2	
F ₂							
F	-267.1	-223.0	-209.5	-204.9	-194.5	-186.5	
N ₂							
N	-82.3	-65.9	-60.8	-54.2	-55.7	-58.1	
H ₂							
H	26.7	26.7	26.7	26.7	26.7	26.7	

^a From Ref. [27].

^b Introduced in [27] as reference values.

magnetic response theory expressions lost in ordinary TDDFT.

The second step made in going to the Loc.3 approximation was the use of the 2LM. This is often a good approximation in TDDFT because the fact

that the occupied and unoccupied orbitals see the same potential, and hence the same number of electrons, means that they are prepared to be a good starting point for describing excitations. However, the 2LM will break down when symmetry consid-

TABLE VI
Isotropic shielding σ calculated with the PD91 exchange correlation potential within the IGLO approximation [1].

	Isotropic shielding, σ (ppm)					Ref. value ^b
	PD91				L-CCD ^a	
	UKS	Loc.1	Loc.2	Loc.3		
HCCH						
C	111.8	114.0	114.7	114.1	122.6	121.8
H	30.0	30.0	29.9	30.0	30.6	—
H ₂ CO						
C	-18.5	-9.4	-6.6	-6.0	6.1	8.2
O	-448.0	-399.4	-384.5	-382.9	-418.0	-379.1
H	21.3	21.6	21.7	21.8	22.6	22.4
CH ₄						
C	192.3	193.6	194.0	194.1	198.6	198.9
H	31.4	31.4	31.4	31.5	31.5	31.6
H ₂ O ₂						
O	107.3	118.9	122.5	139.0	133.9	—
H	24.5	24.8	24.9	25.2	25.2	—
NH ₃						
N	262.4	263.9	264.4	263.3	268.8	270.7
H	31.4	31.4	31.4	31.4	31.7	31.6
H ₂ O						
O	327.7	329.9	330.7	329.3	335.4	337.9
H	30.9	30.9	30.9	30.9	25.2	30.9
HNC						
C	14.9	28.1	32.0	41.9	28.5	—
N	93.2	101.8	104.5	110.7	105.5	—
H	27.3	27.3	27.3	27.3	28.3	—
HCN						
C	78.3	83.1	84.6	87.8	84.4	86.3
N	-42.7	-29.3	-25.1	-15.0	-14.4	-13.6
H	28.6	28.6	28.6	28.5	29.4	29.0
CO						
C	-8.3	7.0	11.5	20.9	3.9	5.6
O	-84.8	-60.6	-53.4	-33.7	-57.4	-52.9
HF						
F	407.8	410.1	410.9	409.4	417.6	418.6
H	29.5	29.5	29.4	29.5	29.4	29.2
F ₂						
F	-238.0	-196.7	-183.9	-179.5	-194.5	-186.5
N ₂						
N	-80.7	-64.0	-58.9	-52.3	-55.7	-58.1
H ₂						
H	26.7	26.7	26.7	26.7	26.7	26.7

^a From Ref. [27].

^b Introduced in [27] as reference values.

erations imply that more than two orbitals are needed to describe an excitation or in cases where there is nontrivial correlation due to accidental degeneracies, such as near an avoided crossing.

The results of the calculations on the test molecules, analyzed in Section 4, show that the Loc.3

approximation performs as well as the local approximations Loc.1 and Loc.2 and always better than the UKS approximation, consistent with our theoretical expectations and consistent with our contention that the reason for the good performance of the Loc.1 and Loc.2 approximations in

SOS-DFPT lies in their similarity to the TDDFT-TDA response expression for electronic properties. This general observation seems to be independent of the choice of functional used for evaluating the exchange correlation potential. In the cases where we noticed that the Loc.3 gives less good agreement in comparison with the reference values, compared to the ones obtained with the Loc.1 and Loc.2 approximations, we also suspect a breakdown of the two-level approximation. The critical test of this hypothesis, of course, is to redo the calculations using only the TDA and not the TDA and 2LM. We are already taking steps to remove the restriction imposed by the 2LM and the results will be presented in a future article.

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Appendix A: Linear Response from Time-Dependent Perturbation Theory

We will derive Eqs. (2.1), (2.2), and (2.3), that is, we will show that the linear response of the property described by an operator, \hat{a} , to a time-dependent perturbation,

$$\hat{b}(t) = \hat{b} \cos \omega_0 t, \quad (\text{A1})$$

is

$$\begin{aligned} \partial \langle \hat{a} \rangle(t) = & \left(\sum_{I \neq 0} \frac{2\omega_I \text{Re} \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega_0^2 - \omega_I^2} \right) \cos \omega_0 t \\ & + \left(\sum_{I \neq 0} \frac{2\omega_0 \text{Im} \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega_I^2 - \omega_0^2} \right) \sin \omega_0 t. \quad (\text{A2}) \end{aligned}$$

We will use the Fourier transform convention,

$$f(\omega) = \int_{-\infty}^{+\infty} e^{+i\omega t} f(t) dt$$

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} f(\omega) d\omega. \quad (\text{A3})$$

It is easy to show that

$$\int_{-\infty}^{+\infty} e^{+i\omega t} \cos \omega_0 t dt = \pi [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)]$$

$$\int_{-\infty}^{+\infty} e^{+i\omega t} \sin \omega_0 t dt = \frac{\pi}{i} [\delta(\omega + \omega_0) - \delta(\omega - \omega_0)]$$
(A4)

using the usual mnemonic

$$\int_{-\infty}^{+\infty} e^{+i(\omega \pm \omega_0)t} dt = 2\pi \delta(\omega \pm \omega_0). \quad (\text{A5})$$

And, of course,

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \pi [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)] = \cos \omega_0 t$$

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \frac{\pi}{i} [\delta(\omega + \omega_0) - \delta(\omega - \omega_0)] = \sin \omega_0 t.$$
(A6)

Consider now a system initially in its ground stationary state with time-independent Schrödinger equation,

$$\hat{H}\Psi_I = E_I\Psi_I; \quad I = 0, 1, 2, \dots \quad (\text{A7})$$

Adding the perturbation $\hat{b}(t)$ leads to a time-dependent wave function,

$$\Psi_0(t) = [\Psi_0 + \delta\Psi_0(t) + \dots]e^{-iE_0t}, \quad (\text{A8})$$

where the linear response, $\delta\Psi_0(t)$, is first order in the perturbation, $\hat{b}(t)$. The corresponding linear response of the expectation value of \hat{a} is given by

$$\delta\langle\hat{a}\rangle(t) = \langle\Psi_0|\hat{a}|\delta\Psi_0(t)\rangle + \langle\delta\Psi_0(t)|\hat{a}|\Psi_0\rangle \quad (\text{A9})$$

and its Fourier transform is

$$\delta\langle\hat{a}\rangle(\omega) = \langle\Psi_0|\hat{a}|\delta\Psi_0(\omega)\rangle + \langle\delta\Psi_0(-\omega)|\hat{a}|\Psi_0\rangle \quad (\text{A10})$$

because

$$\int_{-\infty}^{+\infty} e^{+i\omega t} \delta\Psi_0^*(t) dt = \left[\int_{-\infty}^{+\infty} e^{-i\omega t} \delta\Psi_0(t) dt \right]^*$$

$$= [\Psi_0(-\omega)]^*. \quad (\text{A11})$$

Thus, we need only work with the linear response of the wave function and its Fourier transform.

Inserting Eq. (A8) into

$$[\hat{H} + \hat{b}(t)]\Psi_0(t) = i \frac{\partial}{\partial t} \Psi_0(t) \quad (\text{A12})$$

and keeping track of the order of perturbation gives the first-order equation

$$\hat{b}(t)\Psi_0 = \left(i \frac{\partial}{\partial t} - \hat{H} + E_0 \right) \delta\Psi_0(t). \quad (\text{A13})$$

Fourier transforming this gives

$$\hat{b}(\omega)\Psi_0 = \int_{-\infty}^{+\infty} e^{+i\omega t} \left(i \frac{\partial}{\partial t} - \hat{H} + E_0 \right) \delta\Psi_0(t) dt$$

$$= \int_{-\infty}^{+\infty} e^{+i\omega t} (\omega - \hat{H} + E_0) \delta\Psi_0(t) dt$$

$$= (\omega - \hat{H} + E_0) \delta\Psi_0(\omega), \quad (\text{A14})$$

where the passage between the first and second line is via integration by parts. We can now invoke intermediate normalization,

$$\langle\Psi_0|\delta\Psi_0(\omega)\rangle = 0, \quad (\text{A15})$$

expand the first-order wave function,

$$\delta\Psi_0(\omega) = \sum_{I \neq 0} \Psi_I c_{I,0}(\omega), \quad (\text{A16})$$

and follow the usual derivation of time-independent Rayleigh–Schrödinger perturbation theory to obtain

$$\delta\Psi_0(\omega) = \sum_{I \neq 0} \Psi_I \frac{\langle \Psi_I | \hat{b}(\omega) | \Psi_0 \rangle}{\omega - \omega_I}, \quad (\text{A17})$$

where

$$\omega_I = E_I - E_0 \quad (\text{A18})$$

are the excitation energies of the unperturbed system. Inserting Eq. (A17) into Eq. (A10) gives

$$\begin{aligned} \delta\langle \hat{a} \rangle(\omega) &= \sum_{I \neq 0} \frac{\langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b}(\omega) | \Psi_0 \rangle}{\omega - \omega_I} \\ &\quad - \sum_{I \neq 0} \frac{\langle \Psi_0 | \hat{b}(-\omega) | \Psi_I \rangle \langle \Psi_I | \hat{a} | \Psi_0 \rangle}{\omega + \omega_I} \\ &= \sum_{I \neq 0} \frac{\omega_I}{\omega^2 - \omega_I^2} (\langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b}(\omega) | \Psi_0 \rangle \\ &\quad + \langle \Psi_0 | \hat{b}(-\omega) | \Psi_I \rangle \langle \Psi_I | \hat{a} | \Psi_0 \rangle) \\ &\quad + \sum_{I \neq 0} \frac{\omega}{\omega^2 - \omega_I^2} (\langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b}(\omega) | \Psi_0 \rangle \\ &\quad - \langle \Psi_0 | \hat{b}(-\omega) | \Psi_I \rangle \langle \Psi_I | \hat{a} | \Psi_0 \rangle). \quad (\text{A19}) \end{aligned}$$

Because $\hat{b}(\omega) = \hat{b}(-\omega)$ [Eq. (A4)], we have that

$$\begin{aligned} \delta\langle \hat{a} \rangle(\omega) &= \sum_{I \neq 0} \frac{2\omega_I \text{Re} \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b}(\omega) | \Psi_0 \rangle}{\omega^2 - \omega_I^2} \\ &\quad + \sum_{I \neq 0} \frac{2\omega I \text{Im} \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b}(\omega) | \Psi_0 \rangle}{\omega^2 - \omega_I^2}. \quad (\text{A20}) \end{aligned}$$

More explicitly,

$$\begin{aligned} \delta\langle \hat{a} \rangle(\omega) &= \left(\sum_{I \neq 0} \frac{2\omega_I \text{Re} \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega^2 - \omega_I^2} \right. \\ &\quad \left. + \sum_{I \neq 0} \frac{2\omega I \text{Im} \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega^2 - \omega_I^2} \right) \\ &\quad \times \{ \pi [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)] \} \\ &= \left(\sum_{I \neq 0} \frac{2\omega_I \text{Re} \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega_0^2 - \omega_I^2} \right) \end{aligned}$$

$$\begin{aligned} &\times \{ \pi [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)] \} \\ &+ \left(\sum_{I \neq 0} \frac{2\omega_0 \text{Im} \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega_I^2 - \omega_0^2} \right) \\ &\times \left\{ \frac{\pi}{i} [\delta(\omega + \omega_0) - \delta(\omega - \omega_0)] \right\}. \quad (\text{A21}) \end{aligned}$$

Back Fourier transforming

$$\delta\langle \hat{a} \rangle(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \delta\langle \hat{a} \rangle(\omega) d\omega \quad (\text{A22})$$

with the help of Eq. (A6) gives the equation we initially set out to derive, namely, Eq. (A2).

Appendix B: Explicit TDFT Electric and Magnetic Linear Response Expressions in a Finite Basis Set Representation

We consider again the response of the expectation value of an operator \hat{a} to an applied perturbation $\hat{b}(t)$. In terms of the linear response of the density matrix, $\delta\hat{P}$,

$$\delta\langle \hat{a} \rangle(t) = \text{tr} \hat{a} \delta\hat{P}(t) \quad (\text{B1})$$

and

$$\delta\langle \hat{a} \rangle(\omega) = \text{tr} \hat{a} \delta\hat{P}(\omega). \quad (\text{B2})$$

Introducing a finite basis set representation using the molecular orbitals of the unperturbed system

$$a_{rs} = \langle \psi_r | \hat{a} | \psi_s \rangle$$

$$\delta P_{rs}(\omega) = \langle \psi_r | \delta\hat{P}(\omega) | \psi_s \rangle \quad (\text{B3})$$

allows us to rewrite Eq. (A24) as

$$\begin{aligned} \delta\langle \hat{a} \rangle(\omega) &= \sum_{rs} a_{rs}^* \delta P_{rs}(\omega) \\ &= \sum_i \sum_a^{\text{occ virt}} (a_{ia}^* \delta P_{ia}(\omega) + a_{ai}^* \delta P_{ai}(\omega)) \end{aligned}$$

$$\begin{aligned}
 &= \sum_i \sum_a^{\text{occ virt}} [(Rea_{ia} - iIma_{ia})(Re\delta P_{ia}(\omega) \\
 &\quad + iIm\delta P_{ia}(\omega)) + (Rea_{ia} + iIma_{ia})(Re\delta P_{ia}(\omega) \\
 &\quad - iIm\delta P_{ia}(\omega))] \\
 &= 2 \sum_i \sum_a^{\text{occ virt}} Rea_{ia} Re\delta P_{ia}(\omega) \\
 &\quad + 2 \sum_i \sum_a^{\text{occ virt}} Im a_{ia} Im\delta P_{ia}(\omega) \\
 &= 2\bar{a}^+ \delta\bar{P}(\omega) \tag{B4}
 \end{aligned}$$

(where ‘‘occ’’ and ‘‘virt’’ refer, respectively, to indices of occupied and unoccupied orbitals) because the only nonzero matrix elements in the linear response of the density matrix are off diagonal in occupation number. [Note that $Re \delta P_{ia}(\omega)$ and $Im \delta P_{ia}(\omega)$ refer, respectively, to the Fourier transforms of the real and imaginary parts of $\delta P_{ia}(t)$ and *not* to the real and imaginary parts of $\delta P_{ia}(\omega)$.] In the electric case, both \hat{a} and $\hat{b}(t)$ are real valued and

$$\delta\langle\hat{a}\rangle(\omega) = 2\bar{a}^+ Re \delta\bar{P}(\omega). \tag{B5}$$

In the magnetic case, both \hat{a} and $\hat{b}(t)$ are purely imaginary and

$$\delta\langle\hat{a}\rangle(\omega) = \frac{2}{i} \bar{a}^+ Im\delta\bar{P}(\omega). \tag{B6}$$

The objective of this appendix is to show that

$$\left\{ \omega \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} - \begin{bmatrix} A & B \\ B & A \end{bmatrix} \right\} \begin{pmatrix} \delta\bar{P}(\omega) \\ \delta\bar{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} \bar{b}(\omega) \\ \bar{b}^*(\omega) \end{pmatrix} \tag{B7}$$

implies

$$\begin{aligned}
 \delta\langle\hat{a}\rangle(\omega) &= 2\bar{a}^+(A - B)^{1/2} \\
 &\quad \times [\omega^2\mathbf{1} - (A - B)^{1/2}(A + B)(A - B)^{1/2}]^{-1} \\
 &\quad \times (A - B)^{1/2}\bar{b}(\omega) \tag{B8}
 \end{aligned}$$

in the electric case and

$$\begin{aligned}
 \delta\langle\hat{a}\rangle(\omega) &= 2\bar{a}^+(A + B)^{1/2} \\
 &\quad \times [\omega^2\mathbf{1} - (A + B)^{1/2}(A - B)(A + B)^{1/2}]^{-1} \\
 &\quad \times (A + B)^{1/2}\bar{b}(\omega). \tag{B9}
 \end{aligned}$$

in the magnetic case. Note that $\hat{b}^*(\omega)$ is the Fourier transform of $\hat{b}^*(t)$, so that $\hat{b}^*(\omega) = [\hat{b}(-\omega)]^*$.

We first perform a unitary transformation

$$\begin{aligned}
 &\left(\frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \right) \left\{ \omega \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} - \begin{bmatrix} A & B \\ B & A \end{bmatrix} \right\} \left(\frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} \right) \\
 &\quad \times \left(\frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \right) \begin{pmatrix} \delta\bar{P}(\omega) \\ \delta\bar{P}^*(\omega) \end{pmatrix} = \left(\frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \right) \begin{pmatrix} \bar{b}(\omega) \\ \bar{b}^*(\omega) \end{pmatrix} \tag{B10}
 \end{aligned}$$

to obtain

$$\begin{aligned}
 &\left\{ \omega \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} - \begin{bmatrix} A + B & 0 \\ 0 & A - B \end{bmatrix} \right\} \frac{1}{\sqrt{2}} \begin{pmatrix} 2Re\delta\bar{P}(\omega) \\ -2iIm\delta\bar{P}^*(\omega) \end{pmatrix} \\
 &= \frac{1}{\sqrt{2}} \begin{pmatrix} 2Re\bar{b}(\omega) \\ -2iIm\bar{b}^*(\omega) \end{pmatrix}. \tag{B11}
 \end{aligned}$$

In the electric case, $Re\bar{b}(\omega) = \bar{b}(\omega)$ and $Im\bar{b}(\omega) = 0$. Hence,

$$\begin{bmatrix} -(A + B) & \omega\mathbf{1} \\ \omega\mathbf{1} & -(A - B) \end{bmatrix} \begin{pmatrix} Re\delta\bar{P}(\omega) \\ -iIm\delta\bar{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} \bar{b}(\omega) \\ \bar{0} \end{pmatrix} \tag{B12}$$

so

$$-(A + B) Re\delta\bar{P}(\omega) - i\omega Im\delta\bar{P}(\omega) = \bar{b}(\omega) \tag{B13}$$

and

$$\omega Re\delta\bar{P}(\omega) + i(A - B) Im\delta\bar{P}(\omega) = \bar{0}. \tag{B14}$$

Equations (B13) and (B14) are easily solved to eliminate $iIm\delta\bar{P}(\omega)$, yielding

$$[\omega^2(A - B)^{-1} - (A + B)] Re\delta\bar{P}(\omega) = \bar{b}(\omega), \tag{B15}$$

which can be solved to give

$$\begin{aligned}
 Re\delta\bar{P}(\omega) &= (A - B)^{+1/2} [\omega^2\mathbf{1} - (A - B)^{+1/2}(A + B) \\
 &\quad \times (A - B)^{+1/2}]^{-1} \times (A - B)^{+1/2}\bar{b}(\omega) \tag{B16}
 \end{aligned}$$

Inserting into Eq. (B5) proves Eq. (B8).

In the magnetic case, $Re\bar{b}(\omega) = \bar{0}$ and $iIm\bar{b}(\omega) = \bar{b}(\omega)$. Hence,

$$\begin{bmatrix} -(A+B) & \omega \mathbf{1} \\ \omega \mathbf{1} & -(A-B) \end{bmatrix} \begin{pmatrix} \text{Re} \delta \vec{P}(\omega) \\ -i \text{Im} \delta \vec{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} \vec{0} \\ -\vec{b}(\omega) \end{pmatrix} \quad (\text{B17})$$

so

$$-(A+B) \text{Re} \delta \vec{P}(\omega) - i \omega \text{Im} \delta \vec{P}(\omega) = \vec{0} \quad (\text{B18})$$

and

$$\omega \text{Re} \delta \vec{P}(\omega) + i(A-B) \text{Im} \delta \vec{P}(\omega) = -\vec{b}(\omega). \quad (\text{B19})$$

Equations (B18) and (B19) are easily solved to eliminate $\text{Re} \delta \vec{P}(\omega)$, yielding

$$[\omega^2(A+B)^{-1} - (A-B)] i \text{Im} \delta \vec{P}(\omega) = \vec{b}(\omega), \quad (\text{B20})$$

which can be solved to give

$$\begin{aligned} i \text{Im} \delta \vec{P}(\omega) &= (A+B)^{+1/2} [\omega^2 \mathbf{1} - (A+B)^{+1/2} (A-B) \\ &\quad \times (A+B)^{+1/2}]^{-1} \times (A+B)^{+1/2} \vec{b}(\omega) \end{aligned} \quad (\text{B21})$$

Inserting into Eq. (B6) proves Eq. (B9).